E.S.R. Evidence for Deconjugation in the Tetramethylurea Radical Cation

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Photobleaching and other experiments show that the radical species generated on γ-irradiation of Freon solutions of tetramethylurea is the parent radical cation and not the dimethylaminyl radical assigned previously; the e.s.r. parameters and other properties of this cation are consistent with a $^2A'$ nitrogen-centred radical formed by twisting one of the NMe_2 groups perpendicular to the molecular plane.

Although the formation of radical cations in the solid state by means of the Freon ($CFCl_3$) radiolysis technique[1,2] is sometimes accompanied by structural rearrangements such as ring opening[3] or hydrogen transfer,[4,5] changes involving deconjugation in a π-electron system have not to our knowledge been described. Here, we present evidence that the radical cation of tetramethylurea (TMU) undergoes such a change to adopt an orthogonal structure. This is in contrast to the recent suggestion by Symons[6] that the cation decomposes at 77 K to the dimethylaminyl radical according to reaction (1).

$$Me_2NCONMe_2^{\cdot +} \rightarrow Me_2NCO^+ + \cdot NMe_2 \qquad (1)$$

The previous assignment of the e.s.r. spectrum from a γ-irradiated solution of TMU in $CFCl_3$ to the $\cdot NMe_2$ radical[6] rested on the agreement between the spectral parameters. Nevertheless, in the course of studies designed to generate the radical cations of 1,3-dimethyluracil and other nitrogen bases, it occurred to us for chemical reasons that the π radical cation of TMU would be unlikely to undergo a σ-bond rupture as in reaction (1). This raised the possibility that the nearly identical

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Table 1. E.s.r. parameters for the dimethylaminyl radical and the radical cations of tetramethylurea, dimethylformamide, dimethylacetamide, and 1,3-dimethylimidazolidin-2-one.

Radical or radical cation	Matrix[a] or solvent	T/K	g-values			Hyperfine couplings/G	Ref.
			$g_{\parallel}$	$g_{\perp}$	$g_{av.}$ or $g_{iso.}$		
$Me_2N\cdot$	$CFCl_2CF_2Cl$	90	2.0017	2.0048		A(6H) 27.0, $A_{\parallel}(^{14}N)$ 41	This work
	$CFCl_2CF_2Cl$	118			2.0040	$A_{iso.}$(6H) 27.3, $A_{iso.}(^{14}N)$ 14.8	This work
	$CH_2CH_2CH_2$	183			2.0044	$A_{iso.}$(6H) 27.36, $A_{iso.}(^{14}N)$ 14.78	10
	H_2O (pH 10.0)	300			2.0044	$A_{iso.}$(6H) 28.48, $A_{iso.}(^{14}N)$ 15.65	11
$Me_2NCONMe_2{}^{\cdot +}$	$CFCl_2CF_2Cl$	84	2.002	2.0042		A(6H) 27.0, $A_{\parallel}(^{14}N)$ 41.6	This work
	$CFCl_3$	81	2.003	2.0043		A(6H) 26.1, $A_{\parallel}(^{14}N)$ 41.8	This work
	$CFCl_3$	77	2.002	2.005		A(6H) 26.5, $A_{\parallel}(^{14}N)$ 42	6
	CF_3CCl_3	81	2.003	2.0043		A(6H) 28.3, $A_{\parallel}(^{14}N)$ 42	This work
	Freon glass[b]	77	2.003	2.0040		A(6H) 28.0, $A_{\parallel}(^{14}N)$ 42.6	This work
$HCONMe_2{}^{\cdot +}$	$CFCl_2CF_2Cl$	82	2.002	2.0043		A(6H) 32.2, $A_{\parallel}(^{14}N)$ 39.6	This work
	$CFCl_3$	81	2.002	2.0045		A(6H) 31.8, $A_{\parallel}(^{14}N)$ 39.6	This work
	$CFCl_3$	77	2.002	2.007		$A_{\parallel}$(6H) 32, $A_{\perp}$(6H) 33 $A_{\parallel}(^{14}N)$ 38	[c]
$MeCONMe_2{}^{\cdot +}$	$CFCl_2CF_2Cl$	82	2.002	2.0042		A(6H) 32.5, $A_{\parallel}(^{14}N)$ 39.7	This work
	$CFCl_3$	81	2.002	2.0044		A(6H) 32.4, $A_{\parallel}(^{14}N)$ 40.0	This work
	$CFCl_3$	77	2.002	2.007		$A_{\parallel}$(6H) 32, $A_{\perp}$(6H) 33 $A_{\parallel}(^{14}N)$ 38	[c]
$CH_2CH_2N(Me)CONMe{}^{\cdot +}$	$CFClCF_2Cl$	84			2.0044	A(6H) 18.4, A(4H) 32.2	This work
	CF_3CCl_3	120			2.0037	A(6H) 18.3, A(4H) 32.3 $A_{\parallel}(2^{14}N)$ 24.9[d]	This work
	$CFCl_2CFCl_2$	135			2.0036	A(6H) 18.4, A(4H) 32.5	This work

[a] Only weak and ill-defined signals were observed from γ-irradiated solutions of 1,3-dimethylimidazolidin-2-one in $CFCl_3$. [b] Equal volumes of $CFCl_3$ and CF_2BrCF_2Br (ref. 16). [c] D. N. Ramakrishna Rao and M. C. R. Symons, *Chem. Phys. Lett.*, 1982, **93**, 495. [d] This value is tentative since the spectrum was dominated by the $M_I(^{14}N) = 0$ lines and the features due to the parallel $M_I(^{14}N) = \pm 1$ and ± 2 components were extremely weak.

parameters resulted from an accidental coincidence in the values for two different radicals, a situation only rarely encountered in e.s.r. spectroscopy.

To facilitate comparison with the radical of interest derived from TMU, the $\cdot NMe_2$ radical was generated by γ-irradiation of a solution of dimethylamine in $CFCl_2CF_2Cl$. Both $Me_2NH^{\cdot +}$ and $\cdot NMe_2$ were formed initially but after annealing to 100 K, the radical cation was converted into the neutral radical by an ion–molecule process,[7] a well known general reaction in this matrix.[8,9] At 120 K the spectrum of $\cdot NMe_2$ became fully isotropic and the parameters agreed with those previously measured in solution[10,11] (Table 1). Figure 1 shows a comparison of the e.s.r. spectrum of the TMU-derived species (a) with that of the $\cdot NMe_2$ radical (b) at *ca.* 80 K in $CFCl_2CF_2Cl$, spectrum (a) being the same as that reported earlier in $CFCl_3$.[6] While spectra (a) and (b) do indeed yield nearly the same e.s.r. parameters (Table 1), the detailed lineshapes are quite different on the low-field side of the spectra. For example, the (+2,+1) and (+3,0) line components are much better resolved in trace (a) than in (b). Such differences are difficult to reconcile with spectra from the same radical.

Clear evidence that these spectra originate from different species comes from the effect of illumination with visible light. As shown in Figure 1, the spectrum derived from TMU is photobleachable whereas that of the $\cdot NMe_2$ radical is unaffected under the same conditions. Similarly, the e.s.r. spectrum obtained from TMU in $CFCl_3$[6] is easily photobleached, verifying that the same TMU-derived radical is generated in both matrices. Moreover, visual examination of these γ-irradiated samples before illumination revealed an intense red colour in the TMU solutions which was also photobleachable whereas there was no colour in the annealed dimethylamine sample that gave the e.s.r. spectrum of $\cdot NMe_2$. Since radical cations often possess strong absorption bands in the visible region,[12] it is more reasonable to consider that the TMU-derived species is the radical cation rather than the $\cdot NMe_2$ radical.

Additional support for the TMU radical cation assignment comes from the observation of an ion–molecule reaction in the $CFCl_2CF_2Cl$ matrix at *ca.* 100 K with the formation of the $\cdot CH_2N(Me)CONMe_2$ radical. Corresponding reactions leading to the familiar triplet e.s.r. spectra of $RCH_2\cdot$ radicals (Table 2) were also observed at about the same temperature for $CFCl_2CF_2Cl$ solutions of the radical cations from dimethylformamide (DMF) and dimethylacetamide (DMA). In every case, the colour (yellow for cations of DMF and DMA) disappeared during the reaction. Furthermore, both the colour centre and e.s.r. spectrum of each of these two amide cations displayed similar photobleaching properties to those described earlier for the TMU species.

As noted by Symons,[6] the fact that the e.s.r. spectrum of the species obtained from TMU shows hyperfine couplings to the nuclei in only one NMe_2 group (Table 1) immediately rules out a planar radical cation‡ in which the unpaired electron would be expected to reside in either of the two closely-spaced (b_1 and a_2) nonbonding π orbitals[13] depicted in (**1a**) and (**1b**).

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‡ Although it is tacitly assumed that neutral TMU, like urea, is planar, the NMe_2 groups could be twisted slightly out of the NCON plane to relieve the steric crowding between the *syn* methyl groups.

Table 2. E.s.r. parameters for $RCH_2\cdot$ radicals produced from tetramethylurea, dimethylformamide, and dimethylacetamide.

Radical	Matrix or solvent	T/K	$g_{av.}$ or $g_{iso.}$	Hyperfine couplings/G	Ref.
$Me_2NCON(Me)CH_2\cdot$	$CFCl_2CF_2Cl$	112	2.0028	$A(2H_\alpha)$ 19.4	This work
$HCON(Me)CH_2\cdot$	$CFCl_2CF_2Cl$	112	2.0027	$A(2H_\alpha)$ 19.6	This work
$MeCON(Me)CH_2$[a]	$CFCl_2CF_2Cl$	110	2.0023	$A(2H_\alpha)$ 19.2	This work
	H_2O (pH 7.0)	289	2.0028	$A_{iso.}(2H_\alpha)$ 18.69, $A_{iso.}(3H_\delta)$ 3.73, $A_{iso.}(^{14}N)$ 1.95	b

[a] The e.s.r. data from the $CFCl_2CF_2Cl$ experiment do not discriminate between the $MeCON(Me)CH_2\cdot$ and $\cdot CH_2CONMe_2$ radicals.
[b] H. Paul and H. Fischer, *Ber. Bunsenges Phys. Chem.*, 1969, **73**, 972.

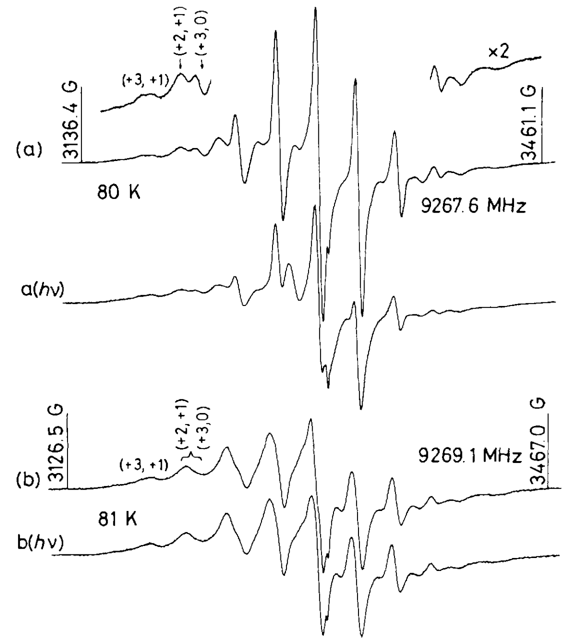
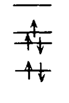
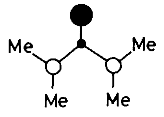
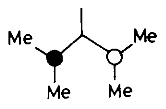


Figure 1. First-derivative e.s.r. spectra of the tetramethylurea radical cation [a and a($h\nu$)] and dimethylaminyl radical [b and b($h\nu$)] recorded under the same instrumental conditions (power, 20 dB) before and after *in situ* illumination of the sample tubes with visible light from a tungsten lamp for 10 min. Certain line components in the low-field portions of the spectra are indicated according to their $M_I(^1H)$, $M_I(^{14}N)$ values, the resonances with non-zero $M_I(^{14}N)$ values being parallel features. The radicals were generated by γ-irradiation of 1 mol % solutions of tetramethylurea and dimethylamine in $CFCl_2CF_2Cl$ at 77 K for doses of 0.4 Mrad, the dimethylamine sample being subsequently annealed to 100 K (see text).

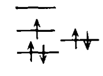


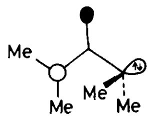


(1a)

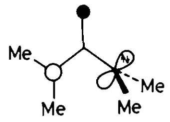


(1b)

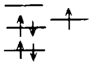


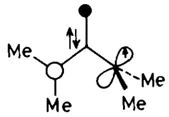


(2a)

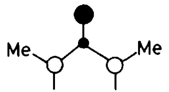


(2b)





(3)



(4)

Consequently, a cation assignment requires a distortion to restrict the spin density to only one NMe_2 group. This is most easily achieved by a deconjugation of one of the NMe_2 groups out of the π system, the cation becoming unsymmetrical so that the spin may reside either in the amido group [structures (**2a**) and (**2b**)] or in the deconjugated NMe_2 group [structure (**3**)], as discussed below.

Our proposal that the TMU cation adopts a deconjugated structure has a corollary. Since a twisted structure of this type cannot be formed in a cyclic urea where the *syn* methyl groups are replaced by methylene groups to form a rigid five-membered ring, an e.s.r. spectrum corresponding to a *delocalized* SOMO either as in structure (**4**) analogous to (**1a**) or as in the cyclic counterpart of (**1b**) should be observed for the cation of 1,3-dimethylimidazolidin-2-one. This is found to be the case, and the e.s.r. parameters are listed in Table 1. On the other hand, a radical cation fragmentation similar to reaction (1) would have given very different e.s.r. results.

Strong *prima facie* evidence therefore exists for a deconjugated TMU cation and it remains to consider which of the alternative structures (**2a**), (**2b**), or (**3**) best represents this species. In structures (**2a**) and (**2b**), the spin is retained in the π system so the driving force for structural change would be determined in part by the tendency for one of the NMe_2 groups to withdraw its 2 electrons from the 4-centre π system and adopt a closed-shell configuration at nitrogen. Except for possible steric effects, (**2a**) should be favoured over (**2b**) since

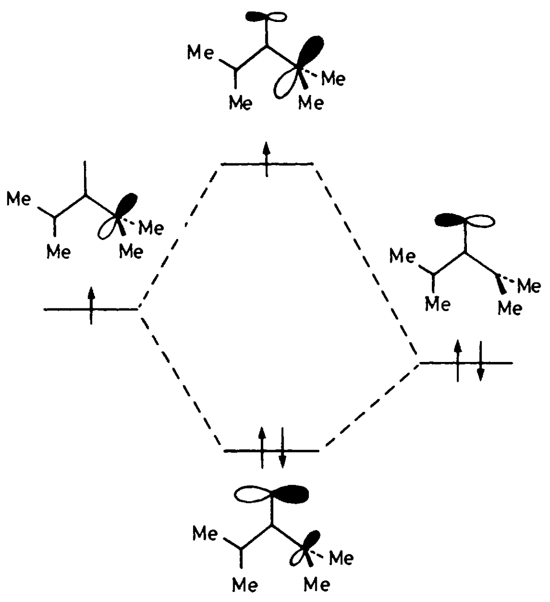


Figure 2. A qualitative MO energy-level diagram to illustrate the mixing of the two high-lying A′ orbitals in the deconjugated form of the tetramethylurea radical cation.

the pyramidal form of the deconjugated NMe_2 group would be expected to have the lower energy. However, any stabilisation achieved as a result of nitrogen lone-pair formation could be more than offset by the concomitant changes in the amide portion of the TMU cation. In particular, recent semi-empirical calculations by Nelsen[14] show that the resonance energy for an amide radical cation is relatively small compared to that for the parent amide. This form of destabilization argues strongly against these pseudoallylic structures (**2a**) and (**2b**) relative to (**3**). Moreover, although the e.s.r. data are not decisive, the hyperfine parameters for $TMU^{\cdot+}$ are sufficiently different from the nearly identical values obtained for the DMF and DMA cations (Table 1), the ^1H coupling being smaller whereas the ^{14}N coupling is larger, to question seriously the assignment of a similar SOMO for all three cations, as is implied by structures (**2a**) and (**2b**).

Turning to (**3**), it would seem at first sight that a cation of this kind should be characterized by larger ^1H and ^{14}N couplings than those observed for $TMU^{\cdot+}$. For instance, on the basis of the isotropic values for the prototype dimethylamine radical cation, namely $a(6H) = 34$ G and $a(^{14}N) = 19.2$ G ($G = 10^{-4}$ T),[11,15] one might have expected a similar ^1H coupling and an $A_{\parallel}(^{14}N)$ value of 47–57 G for this $Me_2N^{\cdot+}-CONMe_2$ structure in the solid state assuming that the undetectable perpendicular ^{14}N coupling is less than 5 G. In fact, the results for $TMU^{\cdot+}$ (Table 1) correspond to only about 80% of these 'expected values.' This discrepancy becomes understandable, however, if one takes into account the fact that the nitrogen-centred SOMO will mix with the other high-lying A′ (n_O) orbital centred mainly on oxygen,[13] as shown schematically in Figure 2, the result being to reduce the nitrogen spin density. Moreover, we suggest that the electronic absorption band ($\lambda_{max} = 508 \pm 5$ nm in a Freon glass[16]) responsible for the characteristic red colour of TMU^+ arises from a transition between these A′ orbitals, since both of these high-lying orbitals are present only in the deconjugated TMU cation.

In the process of deconjugation, one of the π orbitals in the planar TMU cation must become the σ orbital on the nitrogen of the twisted NMe_2 group. It would seem that this correlation should be with the nonbonding (a_2) $\pi(N)$ orbital (**1b**). Upon twisting the NMe_2 group, this orbital will change naturally into the SOMO of (**3**) as it becomes increasingly concentrated at this nitrogen and destabilizes as a result of the interaction with the n_O orbital (Figure 2).

We conclude that the TMU radical cation is best described as the orthogonal structure (**3**),[17] which provides an interesting contrast to the symmetrical planar structure of the venerable radical cation of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine known as Würster's blue. Evidently, the availability of a bridging π system is not a sufficient condition to bring about complete delocalisation between two terminal NMe_2 groups in a radical cation. In general, one expects that the higher the centre of gravity for the filled orbitals in the complete π manifold, the more likely it will be for $\pi \rightarrow \sigma$ electron reorganization to reduce such delocalisation.

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